

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
30 October 2003 (30.10.2003)

PCT

(10) International Publication Number
WO 03/089532 A1

(51) International Patent Classification⁷: **C09D 11/00**

(21) International Application Number: **PCT/GB03/00808**

(22) International Filing Date: 27 February 2003 (27.02.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0208865.6 18 April 2002 (18.04.2002) GB

(71) Applicant (for all designated States except US): **AVECIA LIMITED [GB/GB]**; Hexagon House, Blackley, Manchester M9 8ZS (GB).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **PATEL, Prakash [GB/GB]**; PO Box 42, Hexagon House, Blackley, Manchester M9 8ZS (GB). **HORROBIN, Tina, Margaret [GB/GB]**; PO Box 42, Hexagon House, Blackley, Manchester M9 8ZS (GB).

(74) Agents: **MORPETH, Fraser, Forrest et al.**; Avecia Limited, Intellectual Property Group, PO Box 42, Hexagon House, Blackley, Manchester M9 8ZS (GB).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

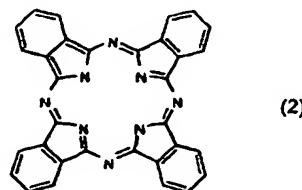
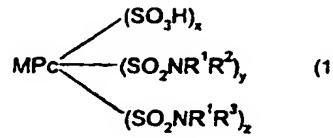
For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

BEST AVAILABLE COPY



(54) Title: PHTHALOCYANINE COMPOUNDS AND INK COMPOSITIONS COMPRISING THE SAME

WO 03/089532 A1



(57) Abstract: A process for coloration of a substrate comprising applying thereto by means of an ink-jet printer an ink composition comprising a compound of Formula (1) or salt thereof, wherein: M is 2H, Si, a metal, an oxymetal group, a hydroxymetal group or a halometal group; Pc is a phthalocyanine nucleus of Formula (2); each R¹ and R² independently are H, C₁₋₄alkyl or C₁₋₄hydroxyalkyl; R³ is phenyl carrying 1 or 2 sulpho substituents or phenyl carrying at least 1 carboxy or 1 phosphato substituent and having further optional substituents; x, y and z are all greater than 0 and the sum of (x+y+z) is 2 to 5. Also novel compounds, compositions, printed substrates and ink-jet printer cartridges.

PHTHALOCYANINE COMPOUNDS AND INK COMPOSITIONS COMPRISING THE SAME

COMPOUNDS, COMPOSITIONS AND USES

This invention relates to compounds, to compositions containing these compounds, to inks, to printing processes, to printed substrates and to ink-jet printer cartridges.

Ink-jet printing is a non-impact printing technique in which droplets of ink are ejected through a fine nozzle onto a substrate without bringing the nozzle into contact with the substrate.

There are many demanding performance requirements for dyes and inks used in ink-jet printing. For example they desirably provide sharp, non-feathered images having good water light and ozone-fastness and optical density. The inks are often required to dry quickly when applied to a substrate to prevent smudging, but they should not form a crust over the tip of an ink-jet nozzle because this will stop the printer from working. The inks should also be stable to storage over time without decomposing or forming a precipitate that could block the fine nozzle.

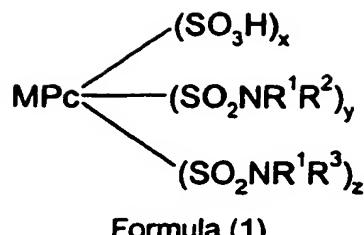
Copper phthalocyanine dyes such as C.I. Direct Blue 199 and C.I. Direct Blue 86, are widely used as colorants in commercial ink-jet printing inks. Other phthalocyanine dyes have also been developed for ink-jet printing such as those in US Patent Number 5,296,023 which describes copper phthalocyanine dyes having sulpho and carboxyphenyl-substituted sulphonamide groups.

With the advent of high-resolution digital cameras it is increasingly common to print off photographs using an ink-jet printer. This avoids the expense of conventional silver halide photography and provides an instant print for the consumer.

The problem of providing an acceptable "photographic quality" ink-jet print presents demanding technical challenge for colourants and inks, in particular with respect to colour-fastness, because photographic quality prints are often kept for many years. It has been found that a key factor in the poor colour-fastness of ink-jet prints is the colorants in the print reacting with oxidising gases, such as ozone, naturally present in the atmosphere.

This invention relates to processes and colorants suitable for use in ink-jet printing able to provide prints with high colour-fastness and ozone-fastness.

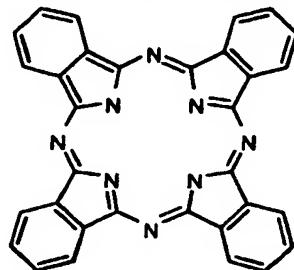
According to the present invention there is provided a process for coloration of a substrate comprising applying thereto by means of an ink-jet printer an ink composition comprising a compound of Formula (1) or salt thereof:



wherein:

5 M is 2H, Si, a metal, an oxymetal group, a hydroxymetal group or a halometal group;

Pc is a phthalocyanine nucleus of Formula (2);



10

Formula (2)

each R¹ and R² independently are H, C₁₋₄alkyl or C₁₋₄hydroxyalkyl;

R³ is phenyl carrying 1 or 2 sulpho substituents or phenyl carrying at least 1 carboxy or 1 phosphato substituent and having further optional substituents;

15 x, y and z are all greater than 0 and the sum of (x+y+z) is 2 to 5.

M is preferably 2Li, 2Na, 2K, Mg, Ca, Ba, Al, Si, Sn, Pb, Rh, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, AlX, GaX, InX or SiX₂, where in X is OH or Cl, more preferably Sc, Ti, Va, Cr, Mn, Fe, Co, Zn, Ni and Cu, especially Cu or Ni.

Preferably R¹ and R² independently are H or methyl, more preferably R¹ and R² are

20 H.

Preferred further optional substituents which may be present on R³ are selected from alkyl, more preferably C₁₋₄-alkyl; alkoxy, more preferably C₁₋₄-alkoxy; polyalkylene oxide; nitro; cyano; sulpho; halo, especially bromo, chloro or fluoro; ureido; SO₂F; hydroxy; ester, more preferably -CO₂(C₁₋₄-alkyl); -NR⁴R⁵; -COR⁴; -CONR⁴R⁵ and -SO₂NR⁴R⁵ wherein R⁴ and R⁵ are each independently H or alkyl, preferably H or C₁₋₄-alkyl.

Preferably R³ is phenyl carrying a single carboxy or sulpho substituent, more preferably R³ is phenyl carrying a single carboxy substituent. It is especially preferred that R³ is 3-carboxy phenyl. Preferably x is 0.2 to 3.8, more preferably 0.5 to 3.5 and especially

25 1 to 3.

30 Preferably y is 0.2 to 3.8, more preferably 0.5 to 3.5 and especially 1 to 3.

Preferably z is 0.2 to 3.8, more preferably 0.5 to 3.5 and especially 1 to 3.

The sum of (x + y + z) is preferably 2 to 4, more preferably 3 to 4.

5 Acid or basic groups on the compounds of Formula (1), particularly acid groups, are preferably in the form of a salt. Thus, the Formulae shown herein include the compounds in free acid and salt form.

10 Preferred salts are alkali metal salts, especially lithium, sodium and potassium, ammonium and substituted ammonium salts (including quaternary amines such as $((\text{CH}_3)_4\text{N}^+$) and mixtures thereof. Especially preferred are salts with sodium, lithium, ammonia and volatile amines, more especially sodium salts. The compounds may be converted to the salt form using known techniques.

15 The compounds of Formula (1) may exist in tautomeric forms other than those shown in this specification. These tautomers are included within the scope of the present invention.

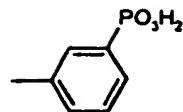
20 The compounds of Formula (1) have attractive, strong cyan shades and are valuable colorants for use in the preparation of ink-jet printing inks. They benefit from a good balance of solubility, storage stability and fastness to water and light. In particular they display excellent colour-fastness, especially ozone-fastness. Furthermore they may be prepared from inexpensive intermediates, avoiding the complexity and expense that is involved in manufacturing some of the more elaborate phthalocyanines.

25 The ink-jet printer preferably applies the ink to the substrate in the form of droplets that are ejected through a small orifice onto the substrate. Preferred ink-jet printers are piezoelectric ink-jet printers and thermal ink-jet printers. In thermal ink-jet printers, programmed pulses of heat are applied to the ink in a reservoir by means of a resistor adjacent to the orifice, thereby causing the ink to be ejected from the orifice in the form of small droplets directed towards the substrate during relative movement between the substrate and the orifice. In piezoelectric ink-jet printers the oscillation of a small crystal causes ejection of the ink from the orifice. Alternately the ink can be ejected by an electromechanical actuator connected to a moveable paddle or plunger, for example as described in International Patent Application WO00/48938 and International Patent Application WO00/55089.

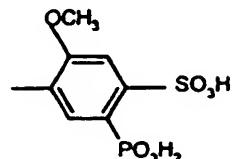
30 The substrate is preferably paper, plastic, a textile, metal or glass, more preferably paper, an overhead projector slide or a textile material, especially paper.

Preferred papers are plain, coated or treated papers which may have an acid, alkaline or neutral character.

35 According to a second aspect of the present invention there is provided a compound of Formula (1) or salt thereof as hereinbefore defined with the proviso that R³ is not of Formula (3), Formula (4) or (5) or a salt thereof:

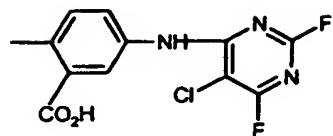


Formula (3)



5

Formula (4)

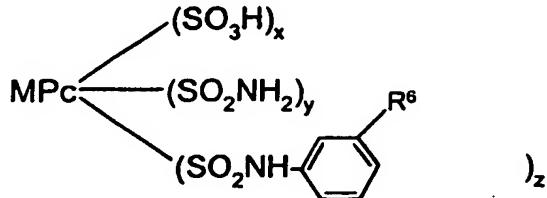


10

Formula (5)

Preferences for compounds of Formula (1) are as described above in relation to the first aspect of the invention.

A particularly preferred compound of Formula (1) is of Formula (6) or a salt thereof:



Formula (6)

20

wherein:

M is 2H, Cu or Ni;

Pc is a phthalocyanine nucleus of Formula (2);

R⁶ is sulpho or carboxy; and

25 x, y and z are all greater than 0 and the sum of $(x+y+z)$ is 2 to 4.

In an especially preferred compound of Formula (6) R⁸ is carboxy.

According to a third aspect of the present invention there is provided a composition comprising a compound according to the second aspect of the invention (preferably of Formula (6)) and a liquid medium.

30 Preferred compositions comprise:

(a) from 0.01 to 30 parts of a compound according to the second aspect of the invention, preferably of Formula (6); and
(b) from 70 to 99.99 parts of a liquid medium;

wherein all parts are by weight and the number of parts of (a)+(b)=100.

5 The number of parts of component (a) is preferably from 0.1 to 20, more preferably from 0.5 to 15, and especially from 1 to 5 parts. The number of parts of component (b) is preferably from 99.9 to 80, more preferably from 99.5 to 85, especially from 99 to 95 parts.

10 Preferably component (a) is completely dissolved in component (b). Preferably component (a) has a solubility in component (b) at 20°C of at least 10%. This allows the preparation of liquid dye concentrates that may be used to prepare more dilute inks and reduces the chance of the dye precipitating if evaporation of the liquid medium occurs during storage.

Preferred liquid media include water, a mixture of water and organic solvent and organic solvent free from water.

15 When the medium comprises a mixture of water and organic solvent, the weight ratio of water to organic solvent is preferably from 99:1 to 1:99, more preferably from 99:1 to 50:50 and especially from 95:5 to 80:20.

It is preferred that the organic solvent present in the mixture of water and organic solvent is a water-miscible organic solvent or a mixture of such solvents. Preferred water-miscible organic solvents include C₁₋₆-alkanols, preferably methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, tert-butanol, n-pentanol, cyclopentanol and cyclohexanol; linear amides, preferably dimethylformamide or dimethylacetamide; ketones and ketone-alcohols, preferably acetone, methyl ether ketone, cyclohexanone and diacetone alcohol; water-miscible ethers, preferably tetrahydrofuran and dioxane; diols, 20 preferably diols having from 2 to 12 carbon atoms, for example pentane-1,5-diol, ethylene glycol, propylene glycol, butylene glycol, pentylene glycol, hexylene glycol and thiodiglycol and oligo- and poly-alkyleneglycols, preferably diethylene glycol, triethylene glycol, polyethylene glycol and polypropylene glycol; triols, preferably glycerol and 1,2,6-hexanetriol; mono-C₁₋₄-alkyl ethers of diols, preferably mono-C₁₋₄-alkyl ethers of diols 25 having 2 to 12 carbon atoms, especially 2-methoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)-ethanol, 2-[2-(2-methoxyethoxy)ethoxy]ethanol, 2-[2-(2-ethoxyethoxy)-ethoxy]-ethanol and ethyleneglycol monoallylether; cyclic amides, preferably 2-pyrrolidone, N-methyl-2-pyrrolidone, N-ethyl-2-pyrrolidone, caprolactam and 1,3-dimethylimidazolidone; 30 cyclic esters, preferably caprolactone; sulphoxides, preferably dimethyl sulphoxide and sulpholane. Preferably the liquid medium comprises water and 2 or more, especially from 2 to 8, water-miscible organic solvents.

Especially preferred water-miscible organic solvents are cyclic amides, especially 2-pyrrolidone, N-methyl-pyrrolidone and N-ethyl-pyrrolidone; diols, especially 1,5-pentane diol, ethyleneglycol, thiodiglycol, diethyleneglycol and triethyleneglycol; and mono- C₁₋₄-alkyl and

C₁₋₄-alkyl ethers of diols, more preferably mono- C₁₋₄-alkyl ethers of diols having 2 to 12 carbon atoms, especially 2-methoxy-2-ethoxy-2-ethoxyethanol.

Examples of further suitable liquid media comprising a mixture of water and one or more organic solvents are described in US 4,963,189, US 4,703,113, US 4,626,284 and EP 5 4,251,50A.

When the liquid medium comprises an organic solvent free from water, (i.e. less than 1% water by weight) the solvent preferably has a boiling point of from 30° to 200°C, more preferably of from 40° to 150°C, especially from 50 to 125°C. The organic solvent may be water-immiscible, water-miscible or a mixture of such solvents. Preferred water-miscible organic solvents are any of the hereinbefore-described water-miscible organic solvents and mixtures thereof. Preferred water-immiscible solvents include, for example, aliphatic hydrocarbons; esters, preferably ethyl acetate; chlorinated hydrocarbons, preferably CH₂Cl₂; and ethers, preferably diethyl ether; and mixtures thereof.

When the liquid medium comprises a water-immiscible organic solvent, preferably a polar solvent is included because this enhances solubility of the compound in the liquid medium. Examples of polar solvents include C₁₋₄-alcohols. In view of the foregoing preferences it is especially preferred that where the liquid medium is an organic solvent free from water it comprises a ketone (especially methyl ethyl ketone) &/or an alcohol (especially a C₁₋₄-alkanol, more especially ethanol or propanol).

The organic solvent free from water may be a single organic solvent or a mixture of two or more organic solvents. It is preferred that when the medium is an organic solvent free from water it is a mixture of 2 to 5 different organic solvents. This allows a medium to be selected that gives good control over the drying characteristics and storage stability.

Liquid media comprising an organic solvent free from water are particularly useful where fast drying times are required and particularly when printing onto hydrophobic and non-absorbent substrates, for example plastics, metal and glass.

The liquid medium may also contain additional components conventionally used in ink-jet printing inks, for example viscosity and surface tension modifiers, corrosion inhibitors, biocides, kogation reducing additives and surfactants which may be ionic or non-ionic.

Although not usually necessary, further colorants may be added to the composition to modify shade and performance properties. Examples of such colorants include C.I.Direct Yellow 86, 132, 142 and 173; C.I.Direct Blue 86, 199, and 307; C.I.Food Black 2; C.I.Direct 35 Black 168 and 195; C.I.Acid Yellow 23; and any of the dyes used in ink-jet printers sold by Seiko Epson Corporation, Hewlett Packard Company, Canon Inc. & Lexmark International. Addition of such further dyes can increase overall solubility leading to less kogation (nozzle blockage) for the resultant ink.

It is preferred that a composition according to the third aspect of the invention is 40 an ink or liquid dye concentrate.

It is especially preferred that the composition according to the third aspect of the invention is an ink suitable for use in an ink-jet printer.

Thus, preferably the composition has a viscosity of less than 20 cP, more preferably less than 10 cP, especially less than 5 cP, at 25°C. These low viscosity compositions are particularly well suited for application to substrates by means of ink-jet printers.

Preferably the composition contains less than 500ppm, more preferably less than 250ppm, especially less than 100ppm, more especially less than 10ppm in total of divalent and trivalent metal ions (other than any divalent and trivalent metal ions bound to a component of the ink).

Preferably the composition has been filtered through a filter having a mean pore size below 10µm, more preferably below 3µm, especially below 2µm, more especially below 1µm. This filtration removes particulate matter that could otherwise block the fine nozzles found in many ink-jet printers.

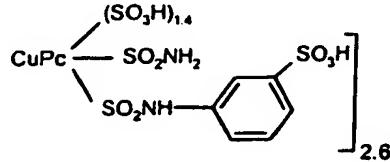
Preferably the composition contains less than 500ppm, more preferably less than 250ppm, especially less than 100ppm, more especially less than 10ppm in total of halide ions.

A fourth aspect of the present invention provides a substrate printed with a composition according to the third aspect of the invention, a compound according to the second aspect of the invention or by means of a process according to first aspect of the invention. Preferably the substrate is paper, plastic, a textile, metal or glass, more preferably paper, an overhead projector slide or a textile material, especially paper more especially plain, coated or treated papers

A fifth aspect of the present invention provides an ink-jet printer cartridge comprising a chamber and an ink wherein the ink is in the chamber and the ink is as defined in the third aspect of the present invention.

The invention is further illustrated by the following Examples in which all parts and percentages are by weight unless otherwise stated.

30 Example 1
Preparation of:



Stage 1

Chlorosulphonic acid (38 ml, 0.57 mole) was charged to a 250ml 4-necked round bottomed flask. POCl₃ (5.3 ml, 0.057 mole) was then added dropwise with continuous mixing over 10-15 minutes while maintaining the temperature below 30°C. This reaction mixture was then stirred for a further 10 minutes. Copper phthalocyanine (14.4g, 0.025 mole) was added in small portions, with stirring, over approximately 45 minutes while

maintaining the temperature below 55 °C. The reaction mixture was stirred for a further 45 minutes and then warmed to 140 ± 2°C over the course of approximately 20 minutes. The reaction mixture was held at this temperature for 4 hours with stirring and was then cooled to room temperature and left to stand overnight.

5 The next morning the reaction mixture was drowned out into ice/water/salt/cHCl (ratio 350g/150ml/12.5g/3.5 ml) whilst maintaining the temperature below 0°C.

The precipitate was collected by filtration and washed with an ice cold saturated brine solution (300 ml).

Stage II

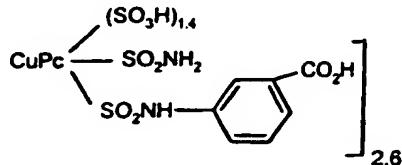
Preparation of the Title Product

10 3-Sulphoaniline (4.46 g, 0.025 mole) was added to a flask containing water (200 ml) and ice (100g) mixture at 0 to 5°C. The product obtained from stage I was added to the flask and the pH was adjusted to the range of pH 7.8 to 8 using a 10% ammonia solution. The reaction mixture was stirred at 0 to 5°C for 3½ hours maintaining the pH at 15 pH 7.8 to 8 by further additions of a 10% ammonia solution. The reaction mixture was then warmed to 40 ± 2°C over 45 minutes and held at this temperature for a further 2 hours. The mixture was then allowed to cool to room temperature overnight.

15 The next morning the pH of the mixture was adjusted to pH 2 using concentrated hydrochloric acid HCl and 20% NaCl w/v (150g) was added. The resultant precipitate was collected by filtration and washed with saturated brine (250 ml). The resultant paste was dissolved in water (800 ml) and the pH adjusted to pH 9 to 9.5 to give a solution. The solution was dialysed with several changes of water over the course of 2 days, then screened through GF/F paper. The filtrate was dried in an oven at 50°C overnight to yield the title product (23.6 g).

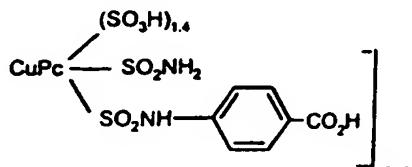
25

Example 2 Preparation of:



30 The title product was prepared by the method described in Example 1 except that in Stage II 3-aminobenzoic acid was used in place of 3-sulphoaniline.

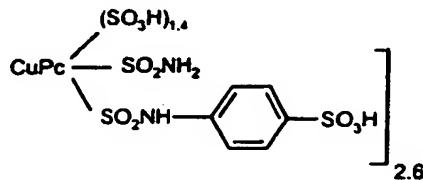
Example 3 Preparation of:



35

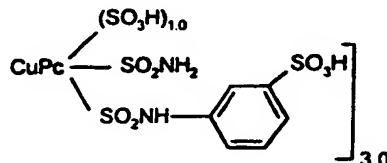
The title product was prepared by the method described in Example 1 except that in Stage II 4-aminobenzoic acid was used in place of 3-sulphoaniline.

5 **Example 4**
Preparation of:



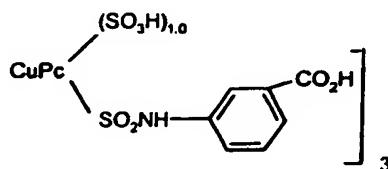
10 The title product was prepared by the method described in Example 1 except that in Stage II 4-sulphoaniline was used in place of 3-sulphoaniline.

Example 5
Preparation of:



15 The title product was prepared by the method described in Example 1 except that the amount of POCl₃ was increased to 8.7 ml, 0.094 mole.

20 **Comparative Example 1**



The title compound was prepared by the method described in Example 3 of US Patent Number 5,296,023 which is incorporated herein by reference thereto.

25 **Example 6**
Preparation of inks

Inks were prepared by dissolving 3.5 parts (by weight) of dye in a solution containing 2-pyrrolidone (2.5 parts), thioglycol (5 parts), urea (2.5 parts), Surfynol™ 465 (1 part, a surfactant commercially available from Air Products Inc.) and distilled water (84.5 parts) and adjusting to pH 8.5 to 9 using sodium hydroxide. The resultant inks were as follows:

Ink 1 contained compound prepared in Example 1 as the dye;
 Ink 2 contained compound prepared in Example 2 as the dye;
 Ink 3 contained compound prepared in Example 3 as the dye;
 Ink 4 contained compound prepared in Example 4 as the dye;
 5 Ink 5 contained compound prepared in Example 5 as the dye;
 Comparative Ink contained the Dye from Comparative Example 1.

Each ink was filtered through a 0.45µm filter and put into a chamber of a Canon trichamber inkjet cartridge.

"Surfynol" is a registered trade mark of Air Products Inc.

10

Example 7 Ink-jet Printing and Properties of the Printed Image

Inks 1 to 5 and the Comparative Ink were printed onto Epson Premium Photo Glossy Paper using an Epson 880 ink-jet printer.

15

Colour Properties of the Prints

The colour properties of the image formed with inks 1 to 5 and the Comparative Ink are shown in Table A.

The CIE colour co-ordinates of each print (a, b, L, Chroma and hue) were measured using a X-Rite 983 Spectrodensitometer with 0°/45° measuring geometry with a spectral range of 400-700nm at 20nm spectral intervals, using illuminant C with a 2° (CIE 1931) observer angle and a density operation of status T. No less than 4 measurements were taken diagonally across a solid colour block on the print with a size greater than 10mm x 10mm.

OD is the optical density of the printed paper, as measured by the X-Rite 983 Spectrodensitometer.

Table A

Ink	%Depth	OD	L	a	b	Hue	Chroma
Control Ink	100	2.51	51	-51	48	223	69
	70	0.86	72	-42	-32	218	52
Ink 1	100	2.11	44	-37	-54	236	66
	70	0.95	67	-37	-39	226	54
Ink 2	100	2.17	44	-39	-53	235	65
	70	0.96	68	-39	-39	225	55
Ink 3	100	2.14	45	-38	-54	235	66
	70	0.98	67	-39	-40	226	55
Ink 4	100	2.19	44	-37	-54	235	66
	70	1.01	66	-39	-40	226	55
Ink 5	100	2.1	45	-40	-52	233	66
	70	0.99	67	-39	-39	226	55

Ozone Fastness

Substrates printed with inks 1 to 5 and the comparative ink were assessed for ozone stability using an ozone test cabinet from Hampden Test Equipment. The test was carried out for two and a half hours at 40°C and 55% relative humidity in the presence of 5 400 parts per hundred million of ozone. Fastness of the printed ink to ozone was judged by the difference in the optical density before and after exposure to ozone using an X-Rite 983 Spectrodensitometer. Thus, the lower the %OD loss the greater the ozone fastness.

Results are shown below in Table B. Table B shows these clearly demonstrate the advantage of inks based on dyes of this invention over the ink containing the 10 comparative dye.

Table B

Ink	Ozone Fastness %OD Loss
Comparative Ink 100% Depth	33
Comparative Ink 70% Depth	42
Ink 1 100% Depth	0
Ink 1 70% Depth	18
Ink 2 100% Depth	2
Ink 2 70% Depth	20
Ink 3 100% Depth	1
Ink 3 70% Depth	19
Ink 4 100% Depth	0
Ink 4 70% Depth	12
Ink 5 100% Depth	0
Ink 5 70% Depth	16

Example 8Further Inks

The inks described in Tables I and II may be prepared wherein the Dye described in the first column is the compound made in the above example of the same number. Numbers quoted in the second column onwards refer to the number of parts of the relevant ingredient and all parts are by weight. The inks may be applied to paper by 20 thermal or piezo ink-jet printing.

The following abbreviations are used in Table I and II:

PG = propylene glycol

DEG = diethylene glycol

NMP = N-methyl pyrrolidone

25 DMK = dimethylketone

IPA = isopropanol

MEOH = methanol

2P = 2-pyrollidone
MIBK = methylisobutyl ketone
P12 = propane-1,2-diol
BDL = butane-2,3-diol
5 CET= cetyl ammonium bromide
PHO = Na₂HPO₄ and
TBT = tertiary butanol
TDG = thioglycol

TABLE I

Dye of Example	Dye Content	Water	PG	DEG	NMP	DMK	NaOH	Na Stearate	IPA	MEOH	2P	MIBK
1	2.0	80	5		6	4				5	1	
2	3.0	90		5	5		0.2				5	
3	10.0	85	3		3							
4	2.1	91		8								
5	3.1	86	5									
1	1.1	81					0.5	0.5	0.2	4		
2	2.5	60	4		15	3			6	10		
3	5	65			20							
4	2.4	75	5		4							
5	4.1	80	3		5	2						
1	3.2	65			5	4						
2	5.1	96			3	2						
3	10.8	90			5	6						
4	10.0	80			2	5						
5	1.8	80			5	4						
1	2.6	84			2	11						
2	3.3	80			2	5						
3	12.0	90			7	10						
4	5.4	69			2	20						
5	6.0	91			4	2						

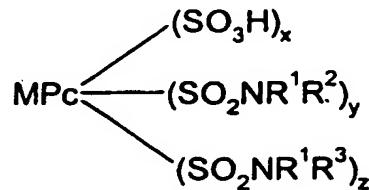
TABLE II

Example	Dye Content	Water	PG	DEG	NMP	CET	TBT	TDG	BDL	PHO	2P	P12
1	3.0	80	15			0.2					5	5
2	9.0	90	5	5		0.15	5.0	0.2		1.2		
3	1.5	85		6	4	0.3			5	0.2		
4	2.5	90	4	8					5		6	6
5	3.1	82			10	5	5		1		4	11
1	0.9	85					0.3		2		3	
2	8.0	90								0.95	5	
3	4.0	70									6	
4	2.2	75									7	
5	10.0	91									5	
1	9.0	76									5	
2	5.0	78									10	
3	5.4	86									12	
4	2.1	70									15	
5	2.0	90									5	
1	2	88									5	
2	5	78									5	
3	8	70									10	
4	10	80									12	
5	10	80									15	
											5	12

Claims

1. A process for coloration of a substrate comprising applying thereto by means of an ink-jet printer an ink composition comprising a compound of Formula (1) or salt thereof:

5

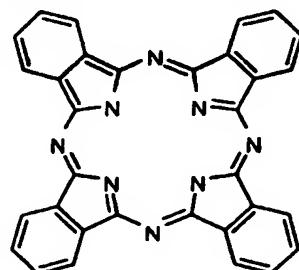


Formula (1)

wherein:

10 M is 2H, Si, a metal, an oxymetal group, a hydroxymetal group or a halometal group;

Pc is a phthalocyanine nucleus of Formula (2);



15

Formula (2)

each R¹ and R² independently are H, C₁₋₄alkyl or C₁₋₄hydroxyalkyl;

R³ is phenyl carrying 1 or 2 sulpho substituents or phenyl carrying at least 1 carboxy or 1 phosphato substituent and having further optional substituents;

20 x, y and z are all greater than 0 and the sum of (x+y+z) is 2 to 5.

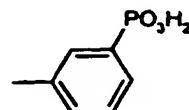
2. A process according to claim 1 wherein M is Cu or Ni.

3. A process according to either claim 1 or claim 2 wherein R³ is phenyl carrying a single carboxy or sulpho substituent.

4. A process according to any one of the preceding claims wherein R³ is 3-carboxy phenyl.

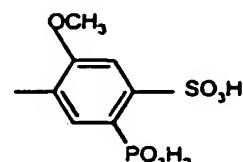
30 5. A process according to any one of the preceding claims wherein the sum of (x + y + z) is 3 to 4.

6. A compound of Formula (1) or salt thereof as defined in claim 1 with the proviso that R³ is not of Formula (3), Formula (4) or (5) or a salt thereof:



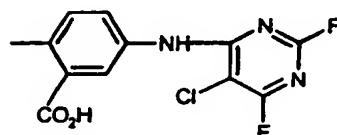
5

Formula (3)



10

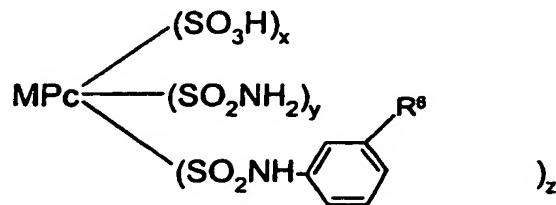
Formula (4)



15

Formula (5).

7. A compound according to claim 6 of Formula (6) or a salt thereof:



20

Formula (6)

wherein:

25

M is 2H, Cu or Ni;

Pc is a phthalocyanine nucleus of Formula (2);

R⁶ is sulpho or carboxy; and

x, y and z are all greater than 0 and the sum of (x+y+z) is 2 to 4.

30

8. A compound of Formula (6) according to claim 7 wherein R⁸ is carboxy.
9. A composition comprising a compound as described in claims 6 to 8 of the invention and a liquid medium.

5

10. A substrate printed by means of a process as described in claims 1 to 5.
11. An ink-jet printer cartridge comprising a chamber and an ink wherein the ink is in the chamber and the ink is a composition as defined in claim 9.

10

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 03/00808

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09D11/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 980 623 A (CHUJO AKIHIKO ET AL) 9 November 1999 (1999-11-09) column 5, line 34 -column 6, line 60 Compound-II-4 column 15 claims 1,7 ----	1-11
X	EP 0 559 309 A (ZENECA LTD) 8 September 1993 (1993-09-08) page 1, line 1 -page 2, line 52 claims 1,3,5,6,8,9; examples 3,6,7 ---- -/-	1-11

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

A document member of the same patent family

Date of the actual completion of the international search

6 May 2003

Date of mailing of the international search report

12/05/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl
Fax: (+31-70) 340-3016

Authorized officer

Zeslawski, W

INTERNATIONAL SEARCH REPORT

Internat'l Application No
PCT/GB 03/00808

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 1997, no. 03, 31 March 1997 (1997-03-31) & JP 08 295819 A (TAOKA CHEM CO LTD;SUMITOMO CHEM CO LTD), 12 November 1996 (1996-11-12) abstract page 3 -page 6 -----	1-11
X	US 6 235 097 B1 (GREGORY PETER ET AL) 22 May 2001 (2001-05-22) column 3, line 50 -column 6, line 63; claims 1,7,8 -----	1-11
X	US 6 221 114 B1 (SENS R UUML DIGER ET AL) 24 April 2001 (2001-04-24) column 1, line 1 -column 2, line 39 column 4, line 10 - line 34; claims 1,5 -----	1-11
X	WO 00 08103 A (SHAWCROSS ANDREW PAUL ;AVECIA LTD (GB); BRADBURY ROY (GB); WRIGHT) 17 February 2000 (2000-02-17) page 1, line 25 -page 4, line 16; claims 1,3,4 -----	1-11
X	US 6 149 722 A (KENWORTHY MARK ET AL) 21 November 2000 (2000-11-21) column 1, line 37 -column 3, line 25; claims 1-3 -----	1-11

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int'l	Application No
PCT/GB	03/00808

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
US 5980623	A	09-11-1999	JP	10212440 A	11-08-1998
			JP	10298463 A	10-11-1998
			JP	11140359 A	25-05-1999
			JP	11158424 A	15-06-1999
EP 0559309	A	08-09-1993	AT	178635 T	15-04-1999
			AU	3100893 A	09-09-1993
			CA	2087490 A1	07-09-1993
			DE	69324291 D1	12-05-1999
			DE	69324291 T2	26-08-1999
			EP	0559309 A2	08-09-1993
			JP	3323261 B2	09-09-2002
			JP	6093196 A	05-04-1994
			US	5296023 A	22-03-1994
JP 08295819	A	12-11-1996	NONE		
US 6235097	B1	22-05-2001	AU	8871398 A	29-03-1999
			EP	1009775 A1	21-06-2000
			WO	9913009 A1	18-03-1999
			JP	2001515943 T	25-09-2001
US 6221114	B1	24-04-2001	DE	19711445 A1	24-09-1998
			DE	19880321 D2	13-07-2000
			WO	9841583 A1	24-09-1998
			JP	2001522384 T	13-11-2001
WO 0008103	A	17-02-2000	AU	5059799 A	28-02-2000
			GB	2354251 A	21-03-2001
			WO	0008103 A1	17-02-2000
			US	6454845 B1	24-09-2002
US 6149722	A	21-11-2000	AU	4278999 A	10-01-2000
			CN	1307617 T	08-08-2001
			EP	1239010 A1	11-09-2002
			EP	1093492 A1	25-04-2001
			WO	9967334 A1	29-12-1999
			JP	2002522561 T	23-07-2002

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- BLACK BORDERS**
- IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- FADED TEXT OR DRAWING**
- BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- SKEWED/SLANTED IMAGES**
- COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- GRAY SCALE DOCUMENTS**
- LINES OR MARKS ON ORIGINAL DOCUMENT**
- REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.